

LECO's GCxGC Utilizing a Consumable-Free Modulator and Second Column Modulation

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NOTE: This document is intended to provide an introduction to LECO's GCxGC system utilizing the Consumable-Free Thermal Modulator. This work will cover differences in hardware and software as compared to LECO's Thermal Modulator using liquid cryogen. It is assumed that the reader is familiar with GCxGC theory and the use of ChromaTOF® software for GCxGC, as covered in, "An Introduction to LECO's Comprehensive Two-Dimensional Gas Chromatography (GCxGC) with ChromaTOF Software".

Introduction

Thermally modulated GCxGC relies on a decrease in temperature in the modulator to focus effluent from the first dimension column. LECO utilizes a dual-stage, quad-jet thermal modulator. For the focusing portion of the modulation process, a jet of dry nitrogen gas is used. The nitrogen gas has been chilled by passing it through a coil immersed in a dewar of liquid nitrogen (LN_2). In the new Consumable-Free Modulator (CFM) option for LECO's GCxGC, the dewar of liquid nitrogen is replaced by a dewar of silicone oil. The silicone oil is chilled by the cold probe from a closed-loop immersion cooler. There are also new control electronics for the CFM.

Hardware

There are several hardware changes associated with the CFM. First, the shape of the cold jets has been changed from a circular jet, to a fan-shaped jet (see Figure 1). The change in shape is intended to focus the chilled nitrogen gas on the column more effectively. This is necessary because the minimum temperature obtainable with the LN_2 -modulated system is -196°C , while the minimum temperature obtainable with the CFM system is only -80°C .

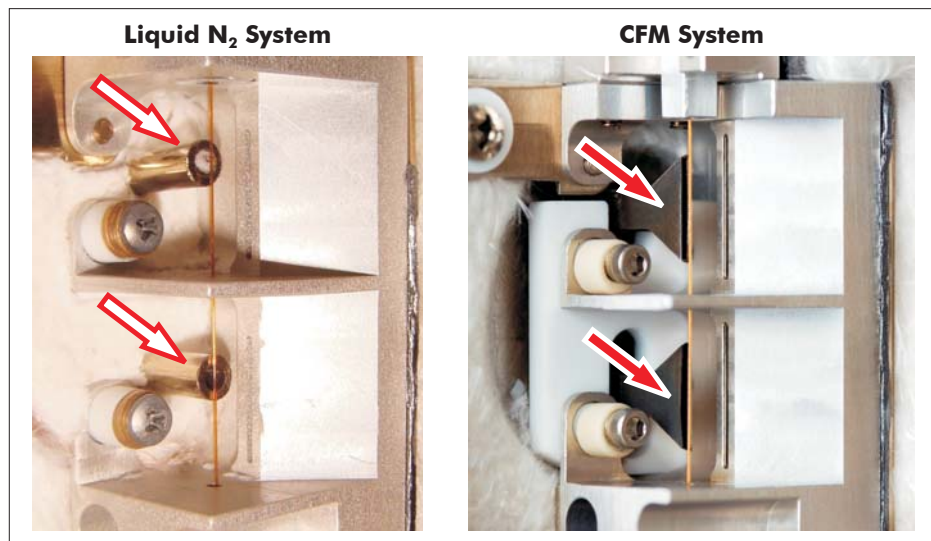


Figure 1: Images highlighting the change in cold jet design from the LN_2 modulator (left) to the CFM (right). The cold jets are indicated by the arrows.

There are also modifications to the modulator block to allow for adjustment of the column alignment. Column alignment is much more critical with the CFM as the narrower cold jets require precise alignment of the column in order to be effective. Instrument specifications require an increase in gas flow to the cold jets. In the LN_2 -modulated system, a flow of 6 liters/minute at 15 psi is mandated. The CFM system is designed for a flow of 10 liters/minute at 15 psi to the cold jets. The requirements for the gas supply to the cold jets are also different for the two systems. The LN_2 -modulated system requires a supply of dry nitrogen gas with a dew point less than or equal to -196°C . The CFM system requires a supply of dry gas with a dew point less than or equal to -73°C and a CO_2 content of less than 1 ppm.

In the system utilizing LN_2 , to chill the cold jets, a dewar system is used. This dewar system consists of a vacuum-insulated "dewar arm" that is connected to an approximately 1.5 liter dewar. The dewar arm houses the coils through which the gas for the cold jets passes to be chilled. The dewar arm is connected to the bottom of the dewar. In this configuration, the dewar arm will fill before the dewar and as the system empties, the dewar will empty before the dewar arm. On the CFM system, the dewar has been removed. The dewar arm and the coils for the cold jet gas it contains are still present. Rather than filling the dewar arm with LN_2 to chill the cold jet gas, the dewar arm is filled with a silicone oil. The cold probe from a

closed-loop immersion cooler is used to chill the silicone oil, which in turn chills the cold jet gas in the coils. Images of the two different dewar systems are shown in Figure 2. Figure 3 shows the closed-loop immersion cooler used in the CFM system.

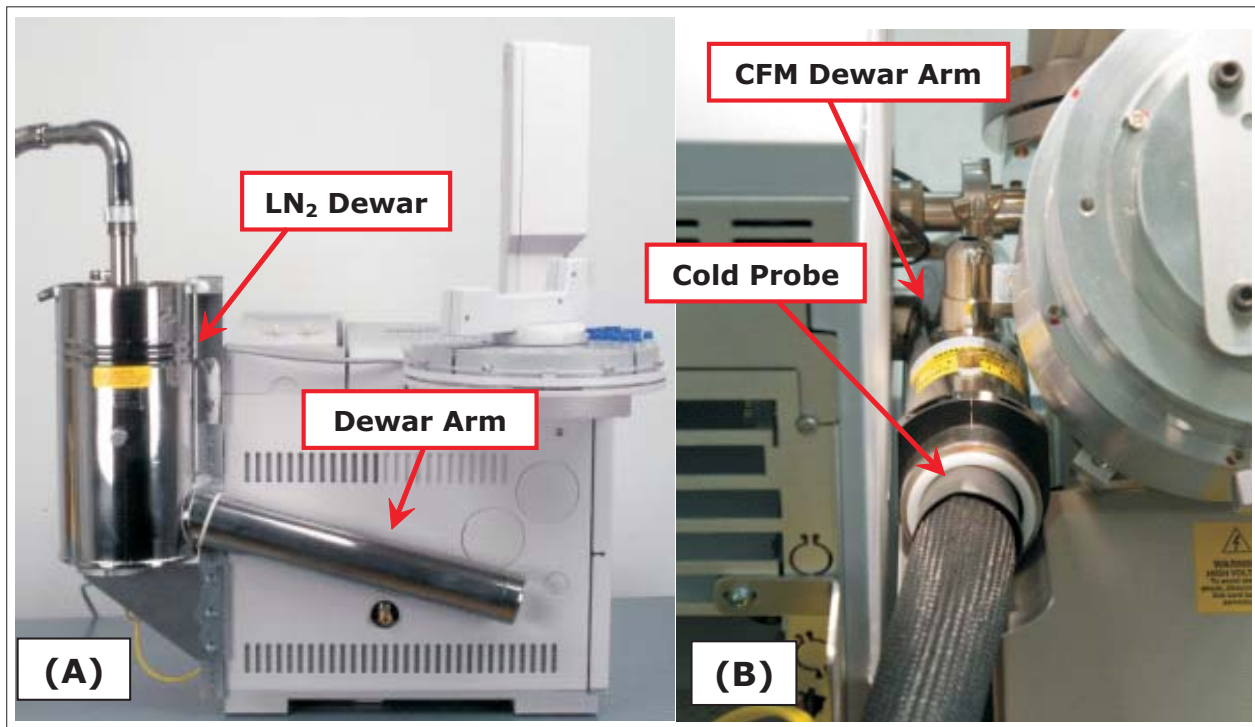


Figure 2: Images of the hardware used to chill the gas for the cold jets in the LN₂ modulator (A) and the CFM (B).



Figure 3: The closed-loop immersion cooler and cold probe utilized in the CFM system.

In addition to the changes in the modulator and chilling mechanisms, there is a major change in the electronics for the CFM. In prior systems, the modulator block temperature, secondary oven temperature and other functions have been controlled as auxiliaries on the GC. In the CFM system, a new external electronics control box is used. Not only does the use of the control box free up auxiliary ports on the GC, it now allows the user to vary parameters that could not be varied in the previous system. These parameters will be discussed in the Software section that follows.

Software

The only changes in the ChromaTOF software are located in the GCxGC Parameters section of the GC Method. The first change now makes it possible to vary the duration of the Hot Pulse during the analysis. The second change allows the user to specify whether the chiller is enabled and at what temperature the closed-loop immersion chiller should be operating.

The external electronics control box allows the analyst to vary the Hot Pulse duration during the analysis. In previous systems, the Hot Pulse duration had to be set to a single duration for the entirety of the analysis. Figure 4 shows the GCxGC Parameters section of the GC Method for a CFM-equipped system utilizing a 5 second Modulation Period with a 600 ms Hot Pulse for the first 750 seconds of the analysis and an 800 ms Hot Pulse for the remainder of the analysis.

Modulation Timing: For 1D GC set second dimension time to 0

#	Start	End	Modulation Period (s)	Hot Pulse Time	Cool Time Between S
1	Start of Run	750 s	5.00	0.60	1.90
2*	750 s	End of Run	5.00	0.80	1.70

Figure 4: An example of the GCxGC Parameters section of the GC Method for a CFM-equipped system utilizing a 5 second Modulation Period with a 600 ms Hot Pulse for the first 750 seconds of the analysis and an 800 ms Hot Pulse for the remainder of the analysis.

For the CFM-equipped system, the GCxGC Parameters section of the GC Method is also where the target temperature for the closed-loop immersion chiller is specified. Figure 5 shows that the Chiller has been enabled and is set to its minimum temperature of -80°C. The Chiller Temperature is not variable during an analysis.

Chiller Enabled

Chiller Temperature:

-80

Figure 5: An example of the GC Method which shows that the Chiller has been enabled and is set to its minimum temperature of -80°C.

Application

LECO describes two column configurations for operation of the GCxGC equipped with the CFM. The first configuration is the high-volatility column configuration (HVCC), where modulation occurs on the end of the first dimension column immediately preceding the connection with the second dimension column. The second configuration is the standard column configuration (SCC), where modulation occurs on the section of the second dimension column immediately following the connection with the first dimension column. The GCxGC system equipped with the LN₂ modulator is operated in the SCC mode.

In the CFM-equipped GCxGC system, the minimum temperature obtainable for the cold jets (-80°C) is significantly higher than that of the LN₂ system (-196°C). The end result is that the CFM system is not able to quantitatively modulate higher volatility compounds as well as the LN₂ system. The specified volatility range for the GCxGC system with the LN₂ modulator is n-C₄ to n-C₄₀. The specified volatility range for the GCxGC system with the CFM is n-C₈ to n-C₄₀. In order to quantitatively modulate n-C₈, the system must be operated in the HVCC. By modulating on the larger I.D. first dimension column, the analyte's linear velocity is lower, thereby increasing the analyte's residence time in the section of the column chilled by the cold jets. This increased residence time enhances the trapping of more volatile compounds. It is important to remember that the modulator serves two competing functions, that of trapping and focusing the analyte, and that of injecting the focused analyte onto the second dimension column. Altering the modulator conditions to improve trapping will result in a decrease in injection performance and vice versa. The increase in trapping efficiency made possible by modulating on the first column results in a decrease in injection performance. Figure 6 shows the linear trends for peak widths of identical analyses of diesel fuel, varying only in the location of modulation and which modulator system was used.

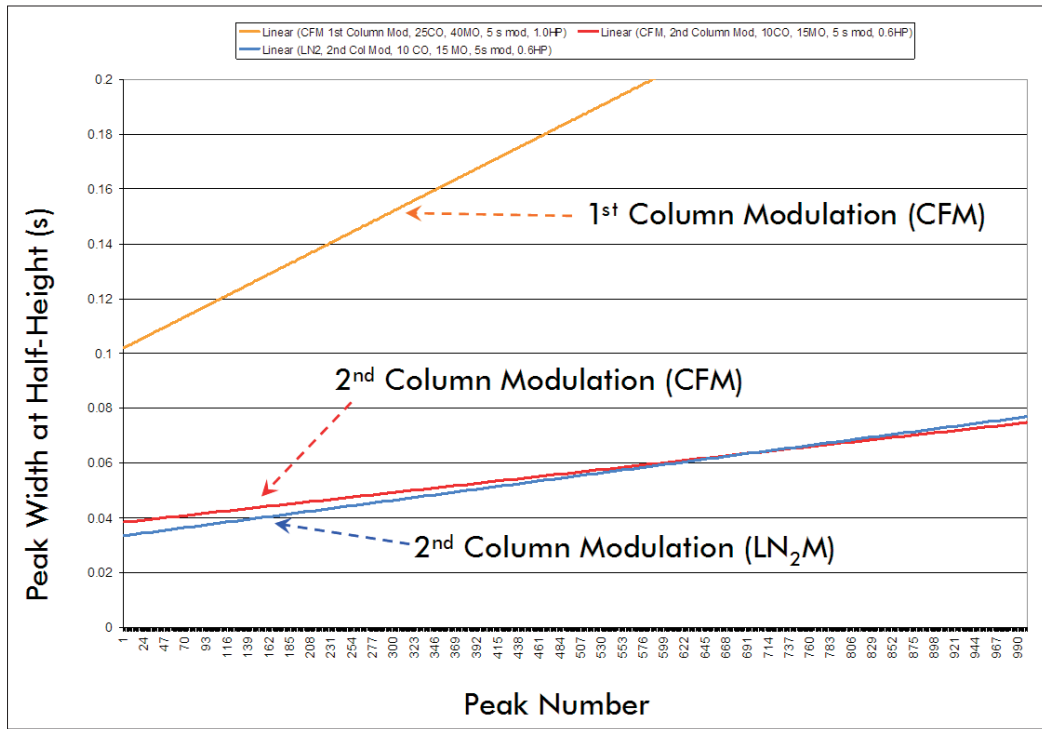


Figure 6: The linear trends for peak widths of identical analyses varying only in the location of modulation and which modulator system was used.

Notice that the analysis run with first column modulation, on the CFM system, has significantly wider peaks than second column modulation on either system and that the peak's width also increases at a faster rate. The increasing peak width is due to two factors. First, the lower linear velocity, which improves trapping efficiency, also means that the focused band is swept from the modulator more slowly. The second cause of wide peaks is due to the fact that the decrease in column diameter occurs after the modulator. The cold jets reduce the temperature of a finite zone of the column in the modulator. The challenge with the HVCC set-up is that the band is focused before the transition from the first dimension column to the second dimension column. This challenge can be described as a volume transfer issue. Ignoring diffusion, the volume of the focused band and the volume of the injection band should be equal. For a band of a fixed volume, if the diameter of the band is decreased, the length of the band must increase. For this example, the length of the focused band, in both cases, will be defined as 5 mm. Figure 7 provides calculated band volumes for commonly utilized sets of column I.D.'s. In the SCC set-up, the band is both focused and injected on the second dimension column, so the focused band length and the injected band length are both 5 mm. In the HVCC set-up, the focused band length is 5 mm and the injected band length varies according to the I.D.'s of the column set being utilized.

**Assuming 5 mm Linear Trapping Zone Regardless of Trapping Location
Assuming No Effects From Diffusion**

Modulated Band Volume

Column ID (mm)	Column Cross-Sectional Area (mm ²)	Band Volume (uL)
0.25	0.0490874	0.245436926
0.18	0.0254469	0.127234502
0.10	0.0078540	0.039269908

$$\text{Band Length} = \frac{V_{C1}}{A_{C2}}$$

1st Column Modulation	2nd Column Band Length (mm)
0.25 mm → 0.18 mm	9.65
0.25 mm → 0.10 mm	31.25
0.18 mm → 0.10 mm	16.20

2nd Column Modulation	2nd Column Band Length (mm)
0.25 mm → 0.18 mm	5.00
0.25 mm → 0.10 mm	5.00
0.18 mm → 0.10 mm	5.00

Column Set	% Increase in Band Length
0.25 mm → 0.18 mm	92.9%
0.25 mm → 0.10 mm	525.0%
0.18 mm → 0.10 mm	224.0%

Figure 7: Calculated injection band volumes for both the SCC and HVCC set-ups. These values demonstrate the increased injected band width when utilizing the CFM in the HVCC set-up. This increased injection band width results in increased peak width, due to volume transfer issues.

Figure 8 provides a visual representation of the increase in injection band width, due to volume transfer, in the case when utilizing a 0.25 mm I.D. column in the first dimension and a 0.10 mm I.D. column in the second dimension. With this particular column set, operation with the HVCC configuration results in a 525% increase in peak width, solely attributable to volume transfer. These values do not account for any band broadening due to other sources.

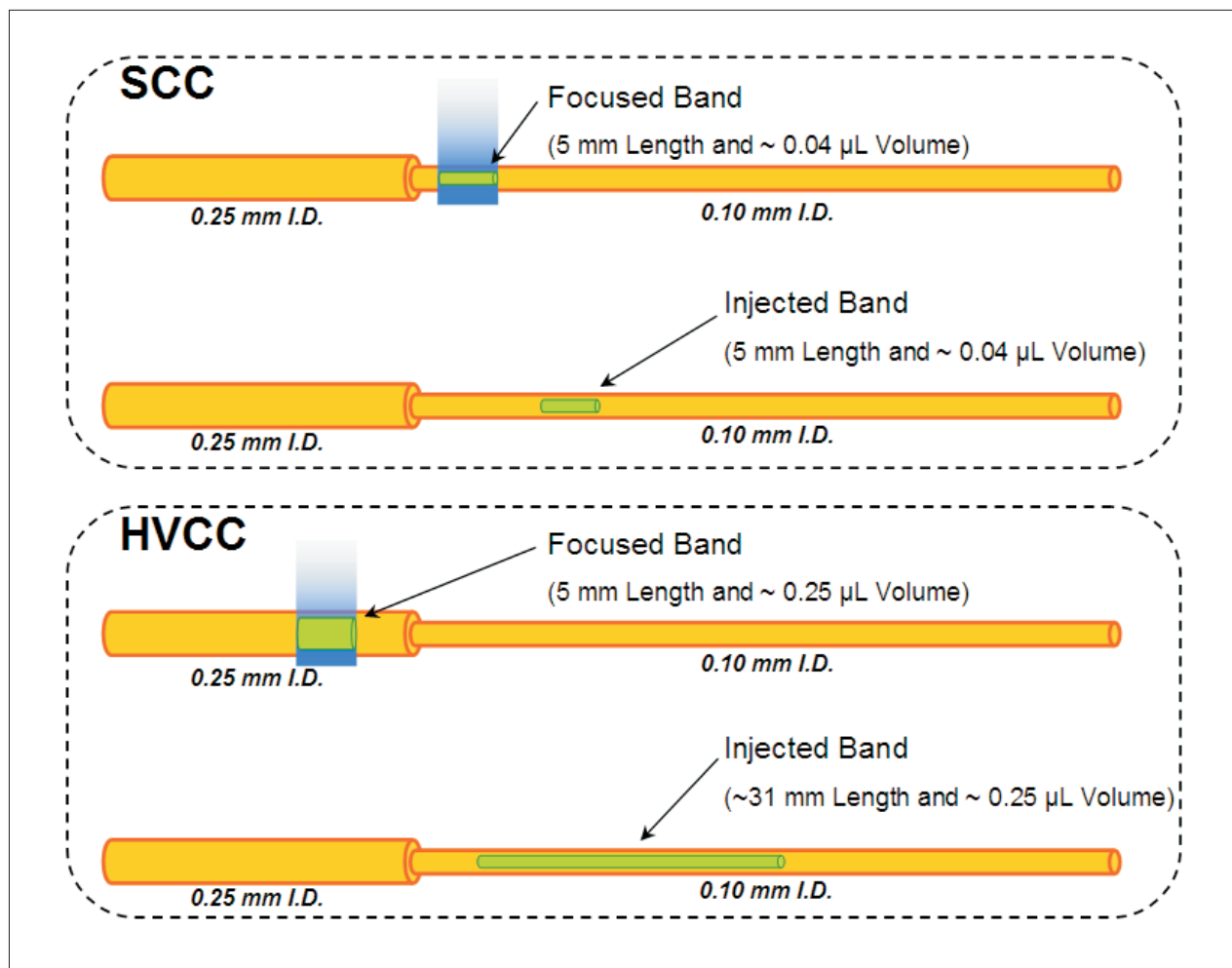


Figure 8: A visual representation of the increase in injection band width due to volume transfer when utilizing a 0.25 mm I.D. column in the first dimension and a 0.10 mm I.D. column in the second dimension. With this particular column set, operation in the HVCC configuration results in a 525% increase in peak width, solely attributable to volume transfer.

The end result of these factors is that when operating the CFM in the HVCC set-up, the ability to trap more volatile species is increased at the cost of increased peak widths. To help minimize the increase in peak widths, the CFM system uses increased column and modulator offsets when operating in the HVCC set-up. These dramatically increased offsets result in a lowered maximum oven temperature for the analysis. The lower maximum oven temperature results in a reduced useable range at the lower volatility end of the range. The rapid increase in peak widths and increased offsets limit the effective useable range of the system from n-C₈ to ~ n-C₂₀ in the HVCC configuration as well as reducing the peak capacity, peak detectability and overall resolution possible when compared to the same analysis run in the SCC set-up. It should be noted that operating in the HVCC set-up is currently the only way to quantitatively modulate compounds with volatilities in the n-C₈ to n-C₁₂ range. The previously discussed challenges with performance of the CFM stem from the fact that the gas for the cold jets does not attain as low of a temperature. This creates challenges when attempting to modulate more volatile species, but could be an advantage when considering less volatile species.

In the LN₂ modulator-equipped GCxGC, the lower cold jet temperature allows quantitative trapping of compounds with volatilities equivalent to that of n-C₄. The same lower cold jet temperature that allows for the trapping of these volatile species creates challenges when the analysis includes less volatile species. When exposed to the very low temperatures of the LN₂-chilled cold jets, less volatile species are focused so effectively that it is difficult to quantitatively desorb them for injection into the second dimension column. The specified upper limit of the useable range, for the LN₂ modulated GCxGC is for volatilities equivalent to n-C₄₀. The higher temperatures used in the CFM system should reduce this and allow the upper limit of the useable range to be extended above n-C₄₀.

A LECO Pegasus 4D (GCxGC-TOFMS) system, equipped with the CFM, with a 30 m x 0.25 mm I.D. x 0.25 μm df Rxi-1 ms in the first dimension and a 1.25 m x 0.10 mm I.D. x 0.10 μm df BPX-50 in the second dimension was set-up in the SCC. The closed loop immersion chiller was set to operate at -80°C . A mixture of n-alkanes from n-C₈ to n-C₄₀ with on-column masses of approximately 2 ng/component was analyzed. Figure 9 shows the linear trace for the modulations of n-tetratetracontane (n-C₄₄). The base-peak has a Full-Width at Half-Height (FWHH) of 133 milliseconds with good peak shape in both the second (individual modulations) and first (blue dashed line) dimensions. This demonstrates excellent characteristics for a compound that had previously been outside of the usable range. The characteristics of n-C₄₄ suggest that we can expect good performance well above n-C₄₅. It should be noted that this performance was accomplished with the closed-loop immersion chiller operating at its minimum temperature of -80°C . If the chiller's operating temperature was increased, enhancement of the performance of less volatile compounds should improve. However, this improvement would be expected to come at the cost of performance with regard to more volatile species.

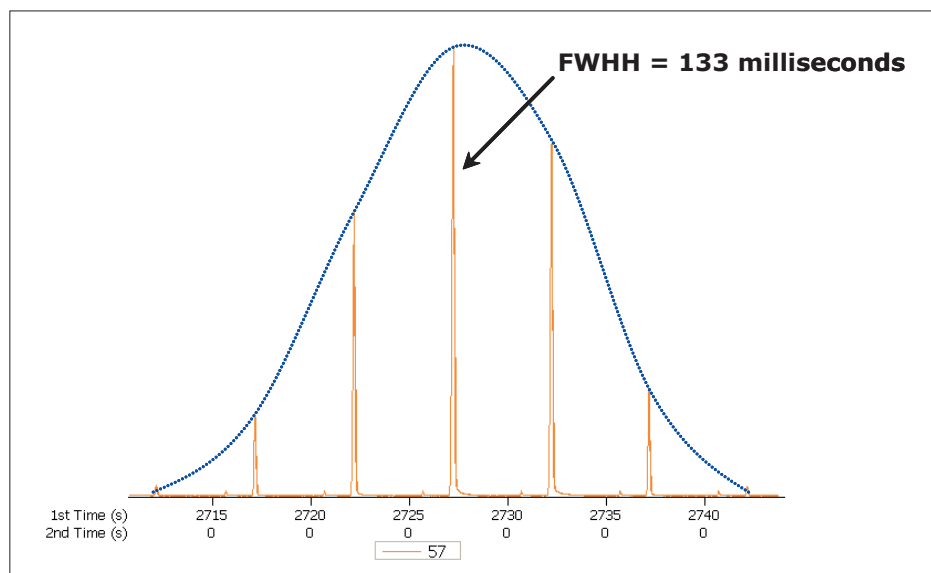


Figure 9: The linear trace for the modulations of n-tetratetracontane (n-C₄₄). The base-peak has a FWHH of 133 milliseconds with good peak shape in both the second (individual modulation) and first (blue dashed line) dimensions.

It has been demonstrated that operation of a CFM-equipped GCxGC system in the SCC shows improved performance for less volatile species. It is important to establish limits of the usable range for this configuration. The CFM-equipped GCxGC system, operated in HVCC has a lower limit for compounds with volatilities equivalent to n-C₈. It is expected that the lower limit of the usable range for the CFM-equipped GCxGC system in the SCC will be above n-C₈.

A series of experiments was conducted to establish the effective lower limit of the usable range. Variables included chiller temperature, hot pulse duration, carrier gas flow, column I.D.'s and whether the hot pulse duration was constant or variable. The experiments were conducted using a series of n-alkanes from n-C₈ to n-C₄₀ and on-column masses/component of approximately 250 pg. Determination of the effectiveness of modulation was made by examining peak shape and plotting peak width at half-height as a function of carbon chain length. Peak shape was determined to fall into one of three categories; modulated, partially-modulated or non-modulated. A peak determined to be modulated exhibited good peak shape with no fronting and is suitable for quantitative work. A peak determined to be partially-modulated exhibited good overall peak shape except for a shallow fronting shoulder resulting from breakthrough beginning to occur in the modulator. It is suitable for qualitative work, but not quantitative work. A non-modulated peak may have a focused section, but the majority of the peak will be broad and unfocused. Figure 10 shows examples of the three categories of modulation effectiveness.

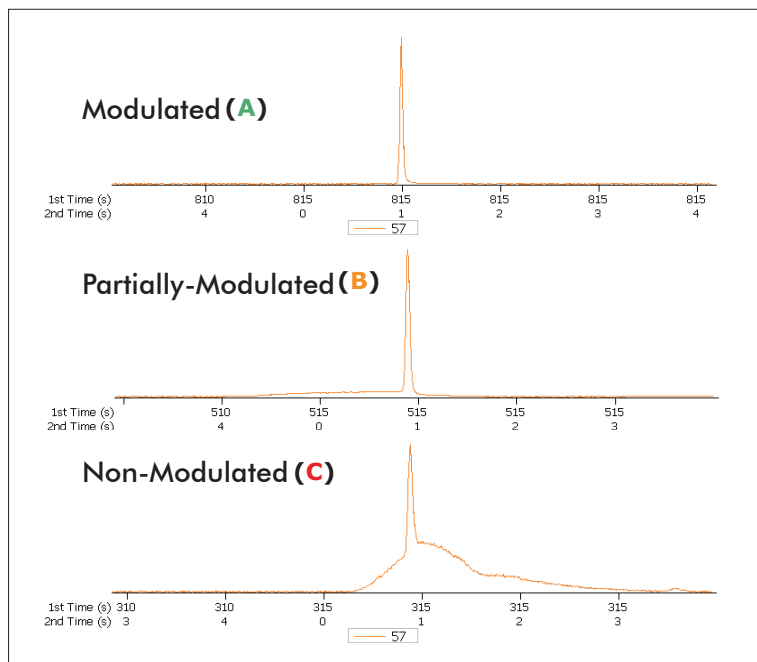


Figure 10: Examples of the three categories of modulation effectiveness. (A) A modulated peak, suitable for quantitative work; (B) A partially-modulated peak, suitable for quantitative work; and (C) a non-modulated peak.

When full-width at half-height is plotted as a function of number of carbons for straight chain alkanes, a distinctively shaped curve is generated. An example of the curve, with points corresponding to the categories of modulation effectiveness, is shown in Figure 11. The shape of the curve will be used to establish the lower limit of modulation effectiveness.

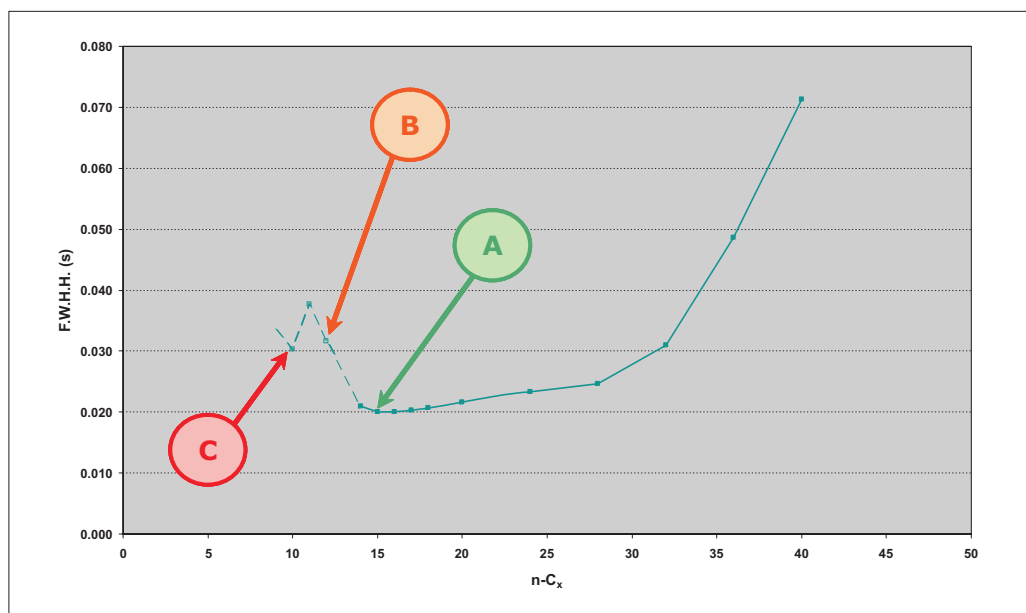


Figure 11: An example of the curve generated when full-width at half-height is plotted as a function of number of carbons for the straight chain alkanes. The indicated points on the curve correspond to the three levels of modulation effectiveness shown in Figure 10.

The most volatile n-alkane able to be quantitatively modulated, utilizing the CFM in SCC, was n-C₁₂. The instrumental set-up used to obtain this was as follows:

- Primary Column: 30 m x 0.25 mm I.D. x 0.25 μ m df Rxi-1 ms
- Secondary Column: 1.25 m x 0.18 mm I.D. x 0.18 μ m df DB-17ms
- Column Flow: 0.8 mL/min Corrected Constant Flow
- Hot Pulse Duration: 800 milliseconds
- Chiller Temperature: -80°C

The experimental curve obtained using this set-up is shown in Figure 12.

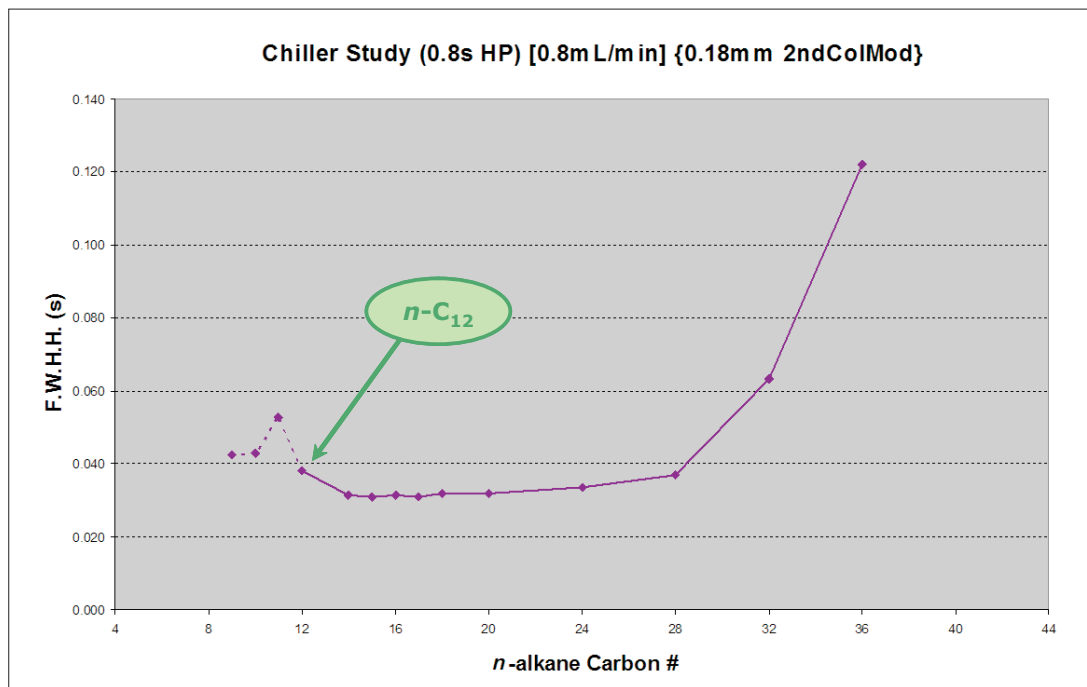


Figure 12: The experimental curve generated from data showing the quantitative modulation of $n\text{-C}_{12}$.

Other observations made during this series of experiments included:

- Decreasing Hot Pulse duration below 600 milliseconds did not improve modulation of more volatile species
- Increasing Hot Pulse duration can improve modulation for less volatile species by improving desorption efficiency
- A smaller difference in column I.D.'s (0.25 mm to 0.18 mm) decreases linear velocity on the second column which improves modulation of more volatile species
- A larger difference in column I.D.'s (0.25 mm to 0.10 mm) increases linear velocity on the second column which improves modulation of less volatile species

It should be noted that improvements in modulation performance at one end of the volatility scale generally come at the cost of degraded performance at the opposite end of the volatility scale. It is a critical part of method development to ensure that there is adequate modulation performance throughout the range of volatilities that will be required for the desired analysis.

Conclusion

Operation of the CFM-equipped GCxGC (in the SCC mode) has been demonstrated to expand the usable range for less volatile species to above the $n\text{-C}_{40}$ upper limit specified for the LN_2 modulator system. This increase in the upper limit of the usable range requires that the system be configured in the Standard Column Configuration (modulating on the beginning of the second dimension column), instead of the High Volatility Column Configuration (modulating on the end of the first dimension column) specified for quantitative modulation of $n\text{-C}_8$. The change from HVCC to SCC increases the lower volatility limit, for quantitative modulation, from $n\text{-C}_8$ to $n\text{-C}_{12}$. It should be noted that these limits for the lower end of the usable range are dependent on factors such as the amount of sample on-column, choice of column set and operating conditions for the system. It is possible that for certain column sets, sample compositions, and operating parameters, the lower limit of the usable range may be higher than $n\text{-C}_{12}$. Thorough method development is necessary to ensure effective operation of the CFM-equipped GCxGC system. If quantitative modulation of species with volatilities between $n\text{-C}_8$ and $n\text{-C}_{12}$ is necessary, the system must be operated in the HVCC set-up. Operation in the HVCC set-up significantly lowers the upper limit of the usable range, when compared to operation in the SCC set-up.

